STUDIES IN MASS TRANSPORT IN CONTACT METAMORPHISM

by

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ABSTRACT

Experiments were performed to observe interactions between natural geological materials via an aqueous vapor phase under hydrothermal conditions. Initial experiments with a granite-and-carbonate system showed that the principal component exchanged between these samples was silica.

New sample materials were chosen in an attempt to "buffer" the experimental system with respect to its major component minerals, in order to observe subtler metasomatic effects among sodium, potassium, and calcium. After heating under pressure, the samples were analyzed for these three elements by atomic absorption spectrophotometry.

The analytical results for these elements show that the difference in concentration between the starting materials and experimental samples was a maximum of ten percent of the initial amounts present, and more often considerably less. The analytical method had a precision sufficient to measure such differences, but uncertainty in weight-loss measurements for the samples, which were part of the experimental technique, prevented quantitative conclusions about the amount of material actually transferred. The primary conclusion is that if any transfer of Ca, Na, or K took place in these experiments, it was too small to be demonstrated by the data presented here.

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II. INTRODUCTION

The controversy over the origin of granites has stimulated considerable interest in laboratory investigations of mineralogical phase relationships and, more recently, laboratory simulations of pressure and temperature conditions thought to approximate field occurrences. As experimental studies demonstrated that "granitic" magmas might be expected at the temperatures and pressures of upper-grade regional metamorphism (Tuttle and Bowen, 1958), a magmatic origin for granites was strongly suggested. Recent broadening of laboratory investigations into simulation of field situations has resulted in interest in metasomatic processes and their possible role in "granitization", porphyroblastesis, and related phenomena.

Luth, Jahns, and Tuttle (in preparation) have begun a series of experiments to consider quantitatively mass transport phenomena, such as those possibly operative in metasomatic processes, in a simulated plutonic environment. This thesis is one segment of the work suggested by them, in which the interactions of natural geologic materials via an aqueous vapor phase are to be observed.

The first rocks studied were samples of the Mount Katahdin (Maine) aplite and the Blair dolomite. The material transported in these experiments was overwhelmingly silica-rich. An attempt was then made to match the silica contents of the two sample materials in order to try to observe the subtler alkali and alkaline earth interactions. The rocks chosen for the bulk of the experimentation were the Mount Airy (North Carolina) granodiorite, and the Spokane argillite (perhaps more appropriately a mildly metamorphosed argillaceous siltstone containing some calcite).

III. REVIEW OF OTHER WORK

P. M. Orville (1963) studied equilibrium relationships between alkali feldspars and a vapor phase containing a two molar solution of alkali chlorides. In studying the invariant three-phase assemblage (at constant pressure) of two alkali feldspars and an alkali chloride solution, he found that the proportion of K to (K+Na) in the vapor phase decreased with falling temperature.

Orville compared his data on vapor-crystal equilibria (1963, figure 11) with data of Yoder, Stewart and Smith (1957; in Orville, 1963, figure 12) and Tuttle and Bowen (1958; in Orville, 1963, figure 12) on melt-crystal alkali distribution curves. He observed a remarkable similarity between the equilibrium of alkali feldspar and alkali chloride solutions and that of alkali feldspar and its water-saturated melt, and concluded that the equilibrium partitioning of alkalies between fluid and crystal phases was apparently unaffected by this radical change in the environment of the alkali ions. This similarity implied that there should be little difference between the molar ratio of alkali feldspars dissolved in a melt and alkali feldspars dissolved in a coexisting vapor phase. Also, the presence of the chloride ion (though justified by natural occurrences in fluid inclusions, etc.) apparently only had a flux-like effect on the attainment of equilibrium.

Orville's Table 2, showing the proportion of K in 2M alkali chloride solution in equilibrium with two alkali feldspars at 2000 bars total pressure, is reproduced below:

Temperature, °C	K/(K+Na), Mole %
670	26.0 ± 0.5
600	23.2 ± 0.5
500	18.5 ± 0.5
400	less than 16.0

This temperature dependence of the alkali ratio suggests a mechanism for alkali metasomatism. Volatiles escaping from a hot crystalline or crystallizing granite into a cooler country rock reach equilibrium with the alkali feldspars in that rock by reducing the proportion of potassium in solution through direct crystallization of K-feldspar or replacement of Na-feldspar.

Orville ran a few tests of this mechanism using a small (30°C over 3 cm.) temperature gradient. He found that the alkali feldspars on the cooler end were indeed enriched in the K-feldspar molecule, normally by five to eight mole percent K/(K+Na) over the bulk composition at the hotter end (Table 3). One experiment with a pure water solution showed very little change, but change in the same direction as the alkali chloride experiments.

Orville also ran some preliminary experiments in the vapor-ternary feldspar system. His experience was that, in the absence of excess silica, the anorthite molecule would not react with alkali chloride solutions. However, it did affect the vapor-feldspar equilibrium by increasing K in the vapor phase relative to Na. In two rocks containing different amounts of anorthite in the plagioclase, equilibration with the same vapor phase would result in depletion of K-feldspar and enrichment of Na-feldspar in the more calcic, and K-enrichment, Na-depletion in the one with less calcic plagioclase.

He noted that gneisses and schists commonly consist of alternating K-feldspar-rich and K-feldspar poor layers. Though this variation is

usually attributed to "metamorphic differentiation", the composition of the plagioclase present is often nearly constant, suggesting a close approach to equilibrium over relatively large volumes of rock. The amount of plagioclase is, however, widely variable. Noting that the CaO and CO_2 contents of shales, clays, and slates (Table 5) are also widely variable, he suggests that formation of anorthite from the different amounts of calcite (probably) in these sedimentary rocks is a likely driving force for K-feldspar differentiation in moderate- to high-grade regional metamorphism.

Luth, Jahns, and Tuttle (in preparation) have also begun some work with the idea of mass transport via the vapor phase. Their experiments were made on the Westerley Granite (G-1) in the presence of an aqueous vapor under the influence of a thermal gradient. Sub-solidus and super-solidus runs were made at pressures of two and ten kilobars.

In all of their experiments with only G-1 in the sample capsule, they observed that silica was the principal component of the dissolved or transported material. They also found that the K/Na ratio of the residual material did not change significantly relative to G-1 at two kilobars pressure and with a thermal gradient of 500°C from the sample to the cold end of the vessel. This result is in contrast to Orville's (1963) experience, but the K/Na changes are so subtle relative to the overwhelmingly silica-rich vapor phase of these experiments that they would not take exception to his results.

At ten kilobars pressure, they noticed the residual material was enriched in potassium relative to sodium at both subsolidus and super-solidus temperatures. This result agrees with those of Orville (1963),

as he observed that an increase in total pressure had the same effect on the equilibrium vapor phase composition as a decrease in temperature; i.e., the K/(K+Na) ratio was lowered (hence the equilibrium solid phase was enriched in K).

In addition to their experiments on pure G-1, Luth, et. al., made some preliminary attempts to evaluate the effects of an inversion in the chemical potential gradient for some of the "components" of the Westerley Granite. Samples of quartz, albite, and microcline (in different experiments) were added to the G-1 capsules, but kept at the cold end of the capsule, mechanically separated from the G-1 sample. The results of these experiments showed that the material transported was indeed "buffered" by the "receptor" samples.

Luth, et. al., concluded by noting that some of their data strongly indicated a two-way flow of material via the vapor phase, from "donor" to"receptor" and vice versa. They emphasized the petrologic importance of a continuously-interacting vapor phase.

IV. DESCRIPTION OF EXPERIMENTS

The general procedure for these experiments was to seal rock samples inside 5-mm. (inside diameter) gold tubing along with some water. The enclosing gold had been heated at 800°C for at least fifteen minutes, then cleaned with six normal hydrochloric acid and rinsed with demineralized water. The water added to the capsules was demineralized, then boiled immediately before loading to drive off CO_2. The capsules were crimped mechanically with a three-cornered drill chuck, then sealed with an electric-arc welder. To prevent vaporization and escape of the water, the capsules were wrapped with wet tissue paper (serving as a heat sink) during welding.

The capsule assembly was then sealed inside a cold-seal pressure vessel and heated at roughly one kilobar pressure for varying lengths of time. Heating was done with resistance-wound furnaces. For the constant-temperature experiments, the furnaces used were set vertically so the pressure vessel could be lowered into and completely surrounded by the heating elements. Measurements with an empty pressure vessel revealed "hot spots" in both constant-T furnaces, but the maximum gradient was no more than 30°C over 5cm. at approximately 630°C. The controllers for the heating elements operated with chromel-alumel thermocouples, but separate chromel-alumel thermocouples monitored the temperature of the sample. The sample couples were in small wells on the outside of the pressure vessel, close to the bottom of the sample chamber. Measurements inside the sample chamber showed that inside and outside temperatures were the same.

For the experiments utilizing a thermal gradient, a special furnace was used which operated with three separately-controlled heating elements,

each 10 cm. long. These elements were arranged end-to-end horizontally and hinged into two equal arcs, so the pressure vessel could be laid inside. Temperature was controlled at the middle of each heating element - at the center of the furnace and at 10 cm. on either side of the center. The pressure vessel used (called a "diffusion bomb") had nine thermocouple wells - one in the center and the others symmetrically placed at 2.5-cm. intervals out to 10 cm. Two capsules were placed in the vessel simultaneously, spaced so they touched at the center thermocouple. Temperature was thus monitored with chromel-alumel thermocouples to a distance of 10 cm. from the center for both. Though no measurements were made, the hinged horizontal arrangement probably resulted in a small circumferential temperature gradient (support for this supposition noted in Appendix I). However, the lengthwise temperature gradient was so much larger, this small imperfection (magnitude maybe 20°C at the hottest point over the bomb length) was ignored.

Pressure was supplied through an air-driven water pump and monitored through gauges in the water line. The gauges had been calibrated with a Heise Bourdon gauge.

The first experiments were with small cores (2.4 mm. in diameter) of the Mt. Katahdin aplite and the Blair dolomite. Several experiments were made at a constant temperature from 650 to 800°C for varying lengths of time; two experiments were done in the presence of a thermal gradient, the maximum temperature being 800°C. The result of these runs was silicification of the outside surface of the dolomite core. The silica-rich vapor phase reacted with the exposed carbonate forming a silicate "crust" from the outer part of the core, the thickness of which was apparently affected by temperature, proximity to the "contact", and

duration of the experiment. X-ray patterns showed the mineralogy of the crust to be calcite and forsterite in the constant temperature runs, and calcite and wollastonite in the experiments utilizing a temperature gradient. The MgO from the dolomite is thought to have gone into recrystallized(?) hornblende found on the surface of the aplite core in the latter two runs. Further details on these experiments are given in Appendix I.

In the aplite-dolomite experiments, the primary component of the material transported by the vapor phase was apparently silica, as was expected from the obvious concentration differential. After the two temperature-gradient experiments, it was decided to change sample materials from the carbonate to a silica-bearing "country rock", the idea being to "buffer" the chemistry of the transport phenomenon by eliminating or greatly reducing the concentration differential for silica. In this way it was hoped that subtler interactions between the alkali and alkaline earth contents, and particularly the alkali and plagioclase feldspar phases of the two sample materials, could be observed.

The rock chosen to replace the dolomite at the cool end of the capsule was the Spokane argillite. This rock would be more appropriately called a mildly metamorphosed argillaceous siltstone, as its mineral phases were quartz, plagioclase feldspar, alkali feldspar, an assortment of micas (including chlorite), and some calcite. The rock had a reddish color in hand specimen, probably due to iron oxide in the cement. The quartz grains had many inclusions, and the feldspar grains were all covered with sericitic material, hence a point count was not attempted. The following is a crude estimate of the mode, based on X-ray diffractometer patterns and study of one thin section:

Quartz	35%
Plagioclase feldspar	20%
Alkali feldspar	15%
Micaceous material (including chlorite, sericite, biotite, etc.)	15%
Calcite	10%

The presence of a small amount of calcite was thought to provide one specific test of Orville's (1963) proposal about calcite content as a driving force for "metamorphic differentiation".

The Mt. Airy granodiorite was also chosen as a substitute for the Mt. Katahdin aplite. This rock was classified petrologically as a "leucogranodiorite" by Dietrich (1961). The observed features and mineralogy of this intrusive body were interpreted by him as indicating formation "by consolidation of an Al-rich, Mg-poor, hydroxyl-fluxed magma under conditions of high pressure" (p. 5). Though the rock body is known to be variable, the average modal analysis as given by him is as follows:

Quartz	20.6%
Plagioclase (An_{20-12})	55.2%
Microcline	19.6%
Biotite	2.5%
Other minerals	3.0%

This rock was chosen as being perhaps more representative of a product of the type of plutonic environment being simulated in the laboratory.

Another modification in technique was suggested by the experience with the constant-temperature dolomite-aplite experiments. The central part of the dolomite core beneath the silicified "crust" was apparently unreacted dolomite. As some residual silica-rich glass was found on the aplite core, reaction between the two phases was assumed not to have gone to completion. As all of the surface area of the dolomite had been silicified, the amount of this area available was assumed to be a rate-limiting factor. Hence, both sample materials were crushed

in a tungsten carbide mortar and ground under acetone in an agate mortar. Thus the amount of surface area available for interaction with the vapor phase was markedly increased in order to expedite attainment of equilibrium.

The gold capsule assembly was modified as follows. Some 2.5 mm. (i. d.) gold tubing was cut into 2.5-cm. lengths, heated and cleaned as described above, then one end was crimped and sealed by welding. Two of these small capsules were carefully weighed; one received a sample of the ground Mt. Airy granodiorite and the other a sample of the ground Spokane argillite. After re-weighing, each capsule was fitted with a gold foil cap, but not sealed. The foil cap was to prevent mechanical removal of the samples to allow a weight-loss calculation, but provide easy access for the vapor. One of these capsules was placed at each end of a 5 mm. gold capsule fifteen cm. long, separated by a spacing rod of 2mm. (i. d.) gold tubing long enough to hold the two small capsules against the ends of the large capsule - normally about nine cm. The amount of free volume inside the large capsule loaded with the smaller ones and the spacer rod was calculated. The specific volume of water vapor at the pressure and temperature of interest (700°C and one kilobar) was obtained from Clark's (1966) Handbook, and a calculation made of the amount of water appropriate to the available volume. One-half to two-thirds of this amount was added to the large capsule, the reduction being made in order to protect the capsule against unexpected drops or surges in the applied pressure, such as those often experienced during quenching. This outer capsule was then sealed by welding. In insertion, the small capsules had been arranged so their open ends (foil caps) were at opposite ends of the large capsule -

hence the vapor had to go around both small capsules to carry atoms from one sample to the other.

Two of the large capsules were placed in the "diffusion bomb", spaced so they touched under the center thermocouple. Pressure was applied, then they were heated for the specified period of time. For one experiment, number 18, a 3.8-cm. capsule was used for the argillite sample, so a larger amount of this material could be added. Atypical example of the arrangement in the furnace for the other experiments is given in Figure IV-1.

A list of water contents, size of samples, etc., is given in Table IV-1. Notice that the temperature given for the "cold" end is the temperature ten cm. from the center, not the argillite sample temperature. The actual argillite sample temperature must be estimated by extrapolation of the temperature gradient.

At the end of the allotted time, the pressure vessel was quenched with a stream of compressed air. The center portion was allowed to cool by radiation to about 500°C (approximately one minute), at which time the pressure was increased to 20,000 psi. Then the air stream was applied, bringing the temperature of the entire bomb to 150°C or less within about five minutes.

The capsule assembly was inspected with a binocular microscope after the run to check for leaks. The weight of the assembly compared to the weight before heating served as a double-check on leaks. The large capsules were then opened, and the sample capsules placed in a dessicator to dry for several days. These small capsules were re-weighed after drying for comparison with the original weights to determine weight loss.

Figure IV-1. Experimental arrangement for run no. 17

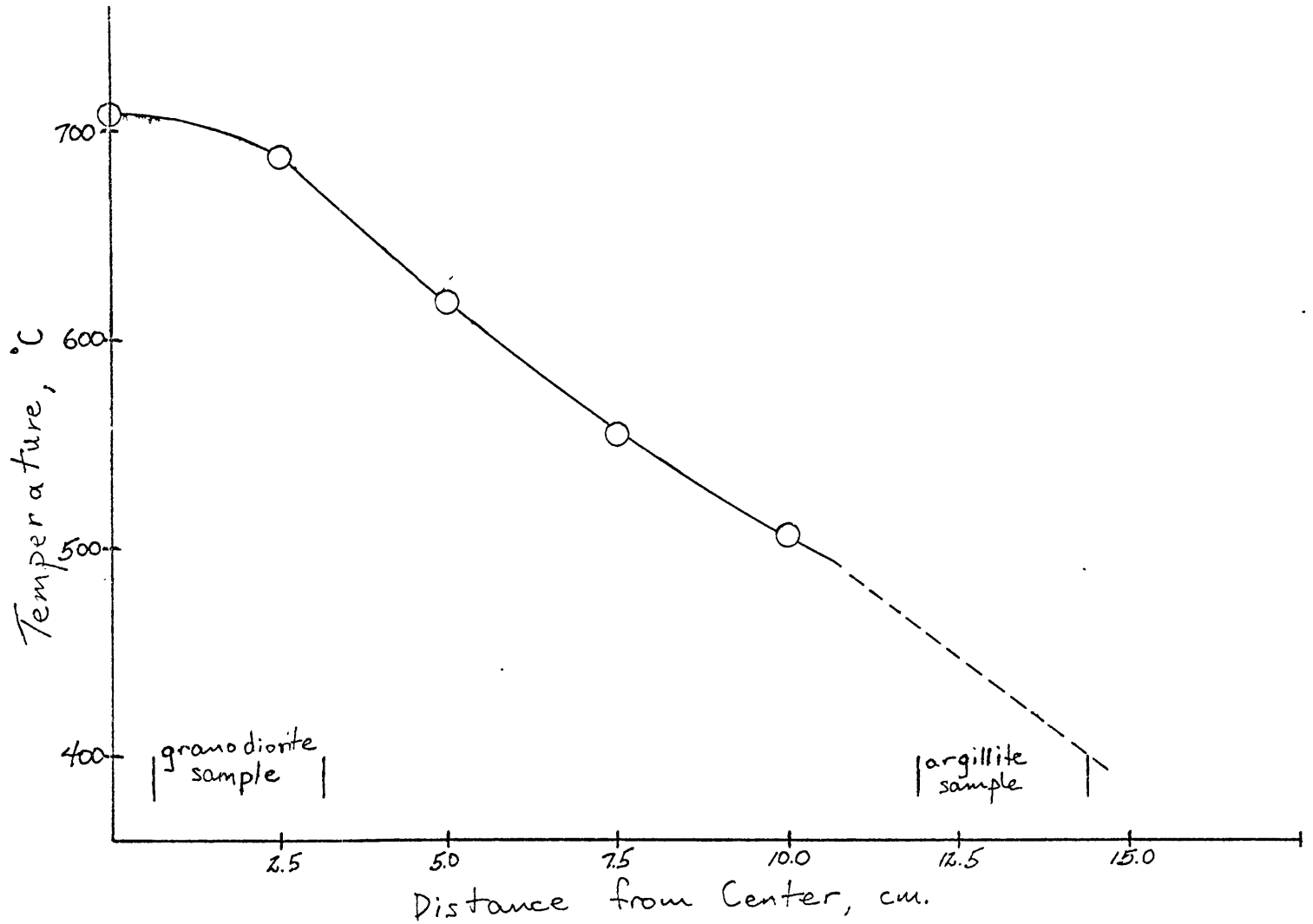


Table IV-1. Description of experiments

Experiment No.	Run length, days	Hot end temp., °C	Cold end temp., °C	Pressure bars	Granodiorite, sample milligrams	Argillite sample milligrams	Water, milligrams
13	10	691±8	511±3	1030	145.26	127.66	191.99
14	10	691±8	503±3	1030	147.44	137.92	428.73
15	8	727±7	576±5	1065	154.74	144.92	461.79
16	8	727±7	530±5	1065	163.18	146.96	409.49
17	19	710±7	505±6	1080	160.49	134.30	433.28
18	19	710±7	504±6	1080	157.19	235.99	449.35

V. ANALYTICAL PROCEDURES AND ACCURACY TESTS

After the heating experiments, the granodiorite and argillite samples were analyzed for sodium, calcium, and potassium. The analyses were done with a Perkin-Elmer Model 303 atomic absorption spectrophotometer. Osram spectral lamps were used as light sources for sodium and potassium, and a hollow-cathode lamp for calcium.

The small capsules were emptied into an agate mortar and ground under acetone to insure homogeneity and reduce any "lumps" which might have formed during heating. Two samples of each capsule's contents were split out, oven dried for at least one hour, carefully weighed, and dissolved according to the procedure given in Appendix II. Appropriate dilutions were made to get the element sought into the correct concentration range for analysis. Reconnaissance tests were made on the spectrophotometer, then the unknown solutions were grouped between standard solutions.

The atomic absorption spectrophotometry method is essentially a light-scattering technique. A light source at a characteristic wavelength for the element sought is focussed into a flame. Unknown and standard solutions are alternately aspirated into the flame, and a measurement of the percent of the light absorbed is made. This quantity, which is exponentially related to the number of absorbing atoms, is converted to a quantity called absorbance which has a linear relationship. A plot of the absorbance vs. concentration, determined by the absorbance values obtained for known standard solutions, yields the concentration of the unknown solution run with the standard. Sample working curves for calcium, sodium, and potassium are given on the next three pages.

Figure V-1. Sample working curve for sodium
(from analyses for sample no. 17-G)

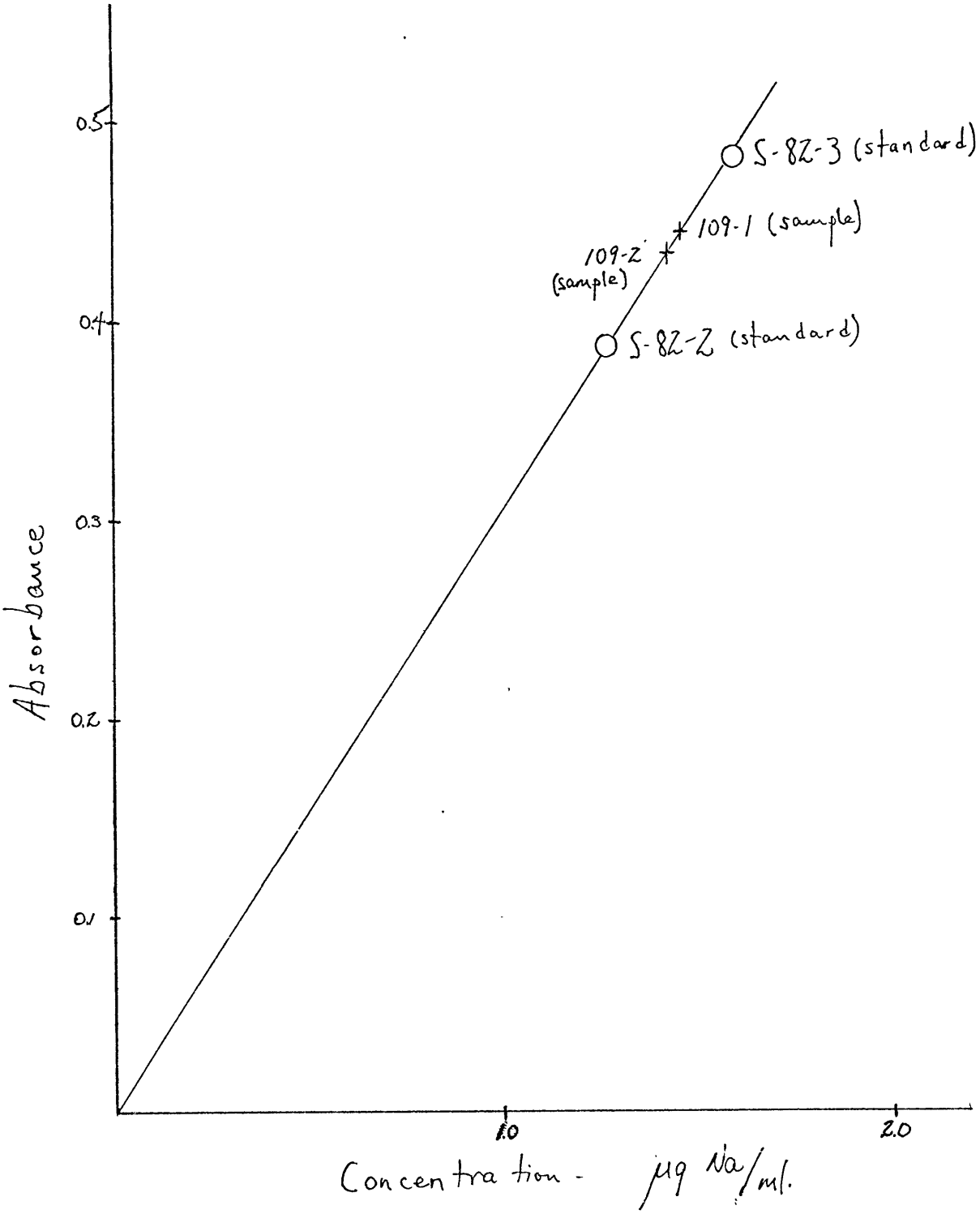


Figure V-2. Sample working curve for potassium (from analyses for sample no. 16-G)

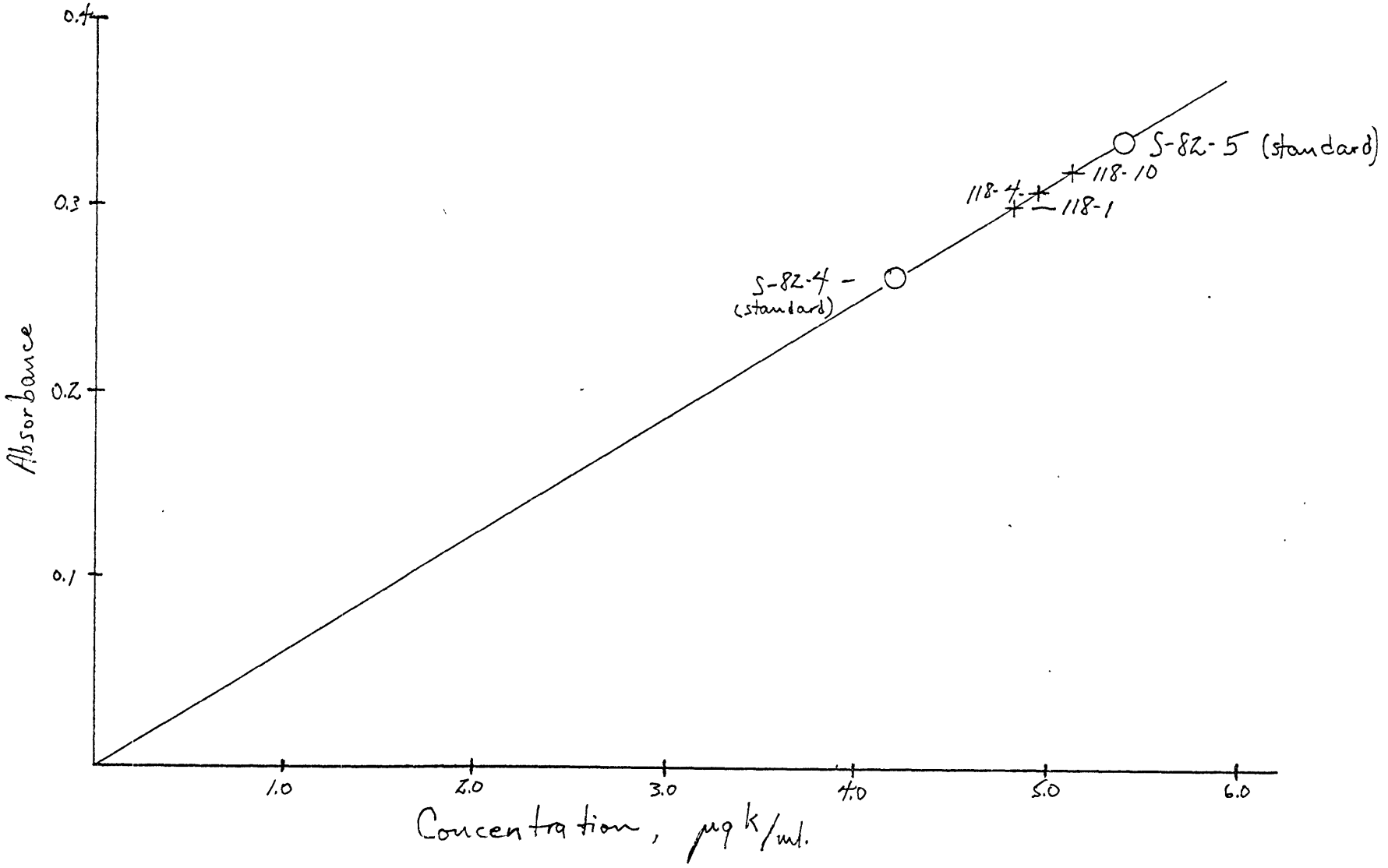
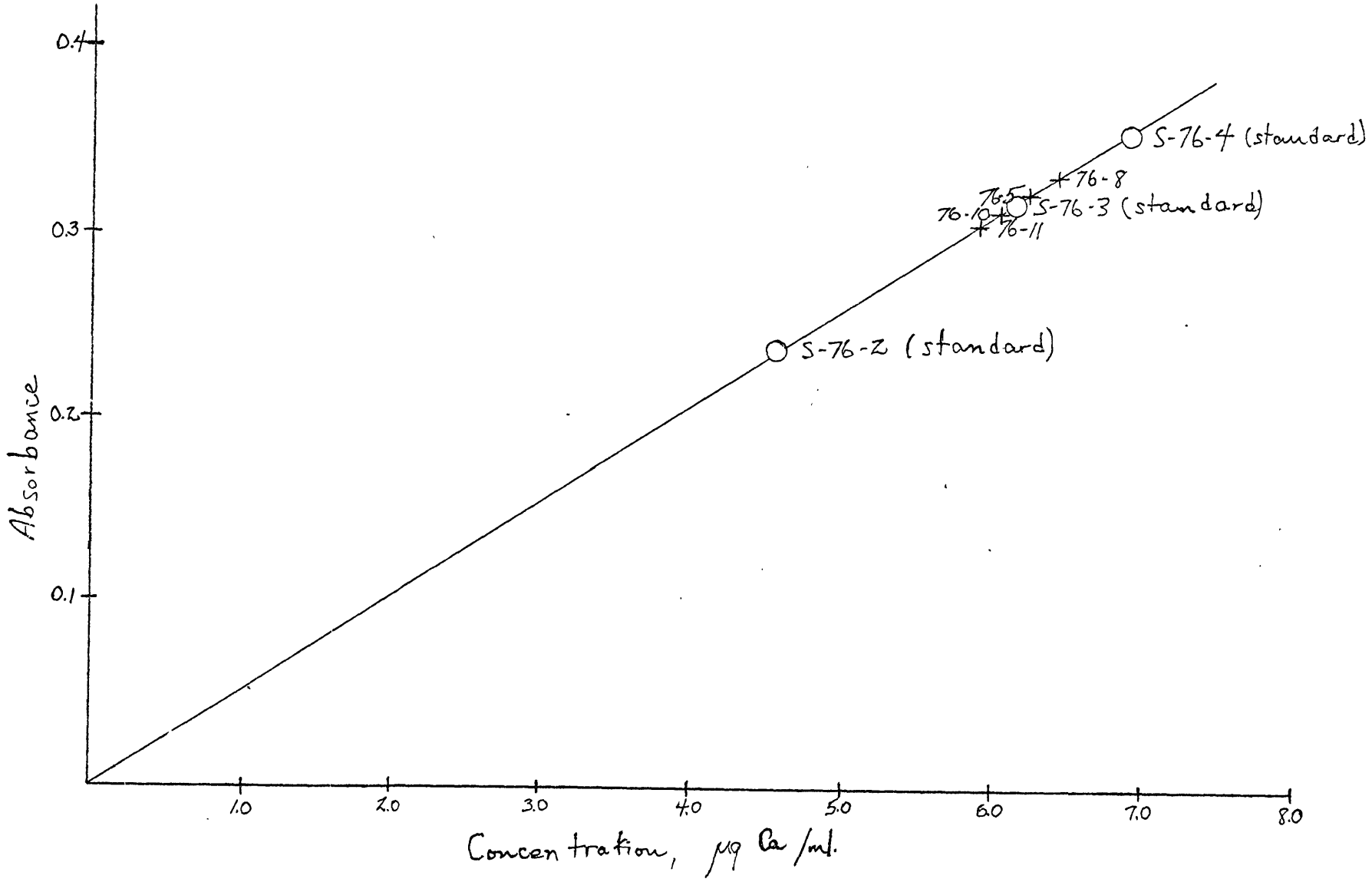


Figure V-3. Sample working curve for calcium (from analysis of several samples)



As with many other methods of analysis, atomic absorption has a matrix effect - i.e., the value obtained for the concentration of an element in a sample is somewhat dependent on what other elements are present, and their concentrations. This matrix effect is minimized by choosing a standard to match the composition of the unknown solutions as closely as possible. The Westerley Granite (G-1) was used as the standard for these analyses. The values used for the elements of interest (aluminum included because of its effect on calcium determinations; see Appendix III) are those preferred by Ingamells and Suhr, as reported by Fleischer (1965):

Al_2O_3	14.08 wt. %, giving	Al	7.450 wt. %
CaO	1.36	Ca	0.972
Na_2O	3.29	Na	2.441
K_2O	5.52	K	4.582 .

(An example of the magnitude of this matrix effect was discovered in some experiments with lanthanum effects on calcium determinations. When G-1 was used as a standard in analyzing W-1 for calcium, the value obtained was about five percent too high. Details on these experiments are given in Appendix III.)

As the chemical changes in the materials studied were expected to be quite small, considerable care was exercised in operation of the analytical instrument and considerable time was devoted to testing accuracy and precision of analyses. The position of the light source and the burner assembly were adjusted for maximum absorption before every set of analyses. Special operating conditions and results of accuracy and precision tests are given for each of the elements of interest below. As the important quantity in these analyses was a change in composition relative to the starting material, a sample of the original granodiorite or argillite was analyzed with each group

of experiment-product samples. The precision (repeatability) of the analyses was emphasized more than the absolute accuracy relative to the analyzed standards.

A. Sodium

Sodium presented the most difficult analytical problems because of the sensitivity of the analytical instrument to the sodium radiation. The low concentration ranges imposed by this sensitivity led to a variable contamination problem. Contamination was monitored by running blanks - solutions to which all the normal reagents had been added and the normal treatments had been applied, but in which no sample was present. Contamination in dissolving the samples was measured to be less than five micrograms. As the sample with the smallest amount of sodium contained at least 250 micrograms of this element, no correction was made to the results for contamination in dissolution.

The sensitivity of the instrument for sodium was such that the optimum concentration range for analysis was one to two micrograms/ml. Thus a given small amount of contamination in diluting a primary solution to this concentration range could result in a significant error. After some standard samples and a few unknown samples had been analyzed, a contamination source in the dilution procedure was discovered. The magnitude of this contamination averaged four micrograms, as measured by comparison of analyses of the same samples before and after elimination of the source. Analyses done prior to this change were thus corrected by a four-microgram reduction (0.08 micrograms/ml. for a 50 ml. dilution), in order to make them comparable to analyses done after the procedural change. The analyses corrected were those for samples 18-A-1, -2, -3, 17-A, and one sample of the argillite starting material

(A note added in support of this correction is that when it is applied to four analyses of the NBS Standard Feldspar No. 99, they average 7.89 wt. % Na, which is closer to the 7.96% value given by the National Bureau of Standards than the 8.13% reported in the table below.).

After the change in dilution procedure, contamination was reduced to normally less than 2.5 micrograms. As it was still somewhat variable, double dilutions were made for most samples, and many of these solutions were determined on the instrument twice. Due to limitations imposed by sample size and amount of primary solution, dilutions for argillite samples produced concentrations in the range 1.0 to 1.5 micrograms/ml., whereas those for the granodiorite samples were in the range 1.5 to 2.0 micrograms/ml. The effect of variable contamination at these concentrations shows in that the confidence limits placed on the sodium analyses for the argillite samples are ± 4%, whereas those for the granodiolite samples are ± 3%. Had the sample size been sufficiently smaller, no dilution would have been necessary, but contamination in dissolving the samples would have been a problem. Had the samples been larger, the larger volume to which the primary solution was diluted might have eliminated the contamination problem in dilution.

Several rock and mineral standards were used to monitor the analyses. The results of analyses for these materials, given in Table V-1, show that accuracy was normally within two percent. The analyses for the NBS Feldspar, Standard Sample No. 99, the Mount Airy granodiorite, and the Spokane argillite are taken as the best tests of precision, as these materials were analyzed the largest number of times. As some of the standard materials were analyzed with two sets of standards (made from two different weighings of G-1), a cross-check on precision was

Table V-1. Sodium analyses for rock and mineral standards, starting materials

Material	Number of weighings/ determinations	Average Na content, weight %	Range of determinations (% of average)	Standard deviation	Value from literature, weight % Na	Reference
G-2, U.S.G.S. Standard Granite	2/4	3.09	0.28 (9.1%)	0.06	3.04	Flanagan (1967, average of two values by "conventional"method)
National Bureau of Standards, Std. Sample No. 99(Soda Feldspar)	4/7	8.13	0.41 (5.0%)	0.05	7.96	NBS Circular 552 (1954)
National Bureau of Standards Std. Sample No. 70(Potash Feldspar)	2/2	1.56	0.06 (3.8%)	0.02	1.77	NBS Analysis with sample bottle(1955?)
Mount Airy Granodionite	5/6	3.70	0.145 (3.9%)	0.02	3.33	Dietrich (1961)
Spokane Argillite	4/5	1.505	0.112	0.02		

provided by the differences between the values obtained for replicate analyses of unknown sample materials. For the argillite samples this difference ranged from 0.3 to 12.7 % of the mean value for the sodium content of the sample, averaging 5.7% (maximum difference 7.9%, average 4.5% without no. 16-A; see note to Table VI-4). The range for the granodiorite samples was 0.3 to 3.5%, averaging 2.0%. As stated above, the range used for assigning confidence limits to reported results for sodium is ± 3% for the granodiorite samples and ± 4% for the argillite samples.

An air-rich flame was found to give maximum sensitivity in sodium analyses.

B. Potassium

A slightly air-rich flame was found to be most efficient for potassium analyses. The best concentration was 4 to 6.5 micrograms/ml. Contamination in dissolving the samples was less than 9 micrograms, whereas the sample containing the least amount of potassium had 580 micrograms, so no correction was applied. Contamination in dilution averaged less than one percent of the concentrations studied, so no correction was applied for that step in the analyses either. The results of analyses for standard materials are given in Table V-2. These results show that agreement was normally within 5%.

The repeated analyses for the Mount Airy granodiorite and the Spokane argillite give a precision of 4% (± 2%). Cross-checking with differences between replicate analyses of unknowns gave a precision range of 0.0 to 4.0 % of the mean value of the two analyses averaging 2.1%. The range used for assigning confidence limits to reported results for K is ± 2%.

Table V-2. Potassium analyses for rock and mineral standards, starting materials

Material	Number of weighings/ determinations	Average k content, weight %	Range of determinations (% of average)	Standard deviation	Value from literature weight % k	Reference
G-2, U.S.G.S. Standard Granite	2/2	3.86	0.4 (1.0%)	0.01	3.70	Flanagan (1967, average of two values by "conventional method)
National Bureau of Standards, Std. Sample No. 99 (Soda Feldspar)	4/4	0.381	0.025 (6.6%)	0.005	0.340	NBS Circular 552 (1954)
National Bureau of Standards, Std. Sample No. 70 (Potash Feldspar)	2/4	10.38	0.58 (5.6%)	0.06	10.44	NBS Analysis with Sample bottle (1955?)
Mount Airy Granodiorite	5/5	2.85	0.11 (3.9%)	0.02	2.72	Dietrich (1961)
Spokane Argillite	3/3	3.81	0.09 (2.4%)	0.02		

C. Calcium

Analyses for calcium were slightly complicated by the presence of aluminum, which complexes the calcium in solution. This problem was avoided by adding a small amount of a lanthanum solution to complex the aluminum. Experiments with Ca/Al and La/Al ratios (Appendix III) showed that the lowest La concentration which could be used was 0.3%.

An acetylene-rich flame was found to be best for Ca determinations. The best concentration range for analysis was 4.5 to 7.0 micrograms/ml. The only appreciable source of contamination was the calcium content of the lanthanum solution added, measured at about 0.2 micrograms/ml. This effect was negated by using the same La concentration in both sample and standard solutions for all analyses.

The results of analysis for standard samples are given in Table V-3. Accuracy was normally within 5%. The repeated analyses for the starting materials gave a precision of 3% ($\pm$ 1.5%). Cross-checking with differences between replicate analyses of unknowns gave a precision range of 0.0 to 3.0 %, averaging 1.2%. The range used for assigning confidence limits to reported results for Ca is $\pm$ 1.5%.

Table V-3. Calcium analyses for rock and mineral standards, starting materials

Material	Number of weightings/ determinations	Average Ca content, weight %	Range of determinations (% of average)	Standard deviation	Value from literature weight % Ca	Reference
G-2, U.S.G.S.	2/2	1.455	0.01 (0.7%)	0.005	1.40	Flanagan (1967, average of two values by "conventional"method)
W-1, U.S.G.S. Standard Diabase	2/10	8.185 (1)	0.30 (3.7%)	0.03	7.805 (1)	Ingannells and Suhr, in Fleischer (1965)
National Bureau of Standards, Std.Sample No. 99 (Soda Feldspar)	2/5	0.225	0.016 (7.1%)	0.002	0.257	NBS Circular 552 (1954)
Mount Airy Granodiorite	4/4	1.19	0.03 (2.5%)	0.01	1.79 (2)	Dietrich (1961)
Spokane Argillite	4/4	1.65	0.02 (1.2%)	0.01		

(1) Poor agreement here is probably due to matrix effects between W-1 and G-1, as the latter was used as the standard for analysis.

(2) The range in these analyses is 1.39 to 2.12 weight % Ca, and none is considered very good--for example, one analysis is from the First Biennial Report of the State Geologist (North Carolina), dated 1893. The Ca content calculated from the norm (by Dietrich) is closer to the present value.

VI. PRESENTATION OF RESULTS

A. X-ray and Microscope

Cursory x-ray and microscopic examinations of the products of experiments 13 and 14 showed slight changes in the physical states of the sample materials. Under the microscope, the argillite was observed to be somewhat "cleaned up" - the sericitic covering of the feldspar grains was removed, and the quartz generally had fewer inclusions than before heating. The original carbonate material was also almost completely removed. No difference was observed for the granodiorite samples.

X-ray diffractometer patterns revealed some subtler changes. For the argillite, the calcite and a mica-region peak (probably sericite) were not present. The alkali feldspar peak at 27.9° 2θ, was also considerably reduced, while the albite peak at 22° was broadened over a larger range of 2θ. There were other minor changes in intensity and position relationships of the plagioclase feldspar peaks in the 23-to-26° region. All of these changes, with the possible exception of the diminution of the alkali feldspar peak, can probably be explained in terms of heating plus assimilation of calcium from the carbonate into the plagioclase feldspar phase. One sample (13-A) was split into two parts which were x-rayed separately. A very slight difference in degree of change was detectable in the relative sizes of the alkali feldspar peak and the relative positions of the plagioclase peaks. The split showing the higher degree of change was that section closest to the unsealed end of the capsule - i.e. the coolest end. Hence, closer access to the vapor may have had some effect.

The changes in the granodiorite shown by x-ray were also minute. There was some homogenization of the plagioclase feldspar, as evidenced

by the peaks in the 23- to-26° 2θ range. The albite peak at 22° was broadened, and the alkali feldspar peak at 21° was resolved slightly from the large quartz peak at 20.85°. These effects are also most likely explained in terms of heating the samples.

B. Weight-loss Data

The results of comparative mearurements of sample weight before and after heating are shown in Table VI-1. The largest loss of weight was 15.84 milligrams (10.74% of initial sample weight). As considerable difficulty was experienced in assuring comparable weights, changes this small are considered to be approaching the limitations of the method.

The experience with the capsule assembly was that, after being heated for the duration of an experiment, some part was always "welded" to something else. Foil caps often stuck to the large enclosing capsule, which in turn was often stuck to the smaller capsule. Also, the foil caps were sometimes coated with a little of the sample material which could not be removed. Another source of uncertainty in the weight mearurements was possible water content in the samples or the starting materials. All drying was done in a dessicator; hence, water might have been held in samples which became highly packed during the experiment.

Within the uncertainty of the analyses, the calcium content did not change for either type of sample during an experiment (see Table VI-2 for Ca analyses below). If the values obtained for calcium content of the samples are taken as correct and compared with calcium content calculated from the value for the starting material adjusted for weight loss, a check on the accuracy of the weight loss measurement can be made.

Table VI-1. Weight loss of samples during experiments

Exp't.No.	Granodiorite			Argillite		
	Sample weight before, milligrams	Sample weight after, milligrams	Weight loss [gain] (as % of original weight)	before, milligrams	after, milligrams	Weight loss [gain] (as % of original weight)
14	147.44	131.60	15.84 (10.74%)	137.92	130.88	7.04 (5.10%)
15	154.74	148.16	6.58 (4.25%)	144.92	140.44	4.48 (3.09%)
16	163.18	159.75	3.43 (2.10%)	146.96	140.79	6.17 (4.20%)
17	160.49	151.97	8.52 (5.31%)	134.30	133.71	0.59 (0.44%)
18	157.19	153.30	3.89 (2.47%)	235.99	228.91	7.08 (3.00%)

As an example, consider the granodiorite sample from experiment 17. If the amount of calcium present, determined by multiplying the initial weight by the calcium concentration in the starting material, is expressed as a percentage of the "reacted" sample weight, a value of 1.26% Ca is obtained. If one milligram is added to this final weight (weight loss reduced by one milligram), that number becomes 1.25%, which agrees precisely with the analytical results. Note, however, that a change of one milligram is more than ten percent of the measured weight loss of 8.52 milligrams. Thus, the numbers for percent weight loss given in the table can only be compared for gross relationships.

The weight-loss data shows no apparent overall trend. For two sets of samples heated for the same length of time (i. e., 15-argillite and -granodiorite are one set; 15 and 16 are two sets heated the same length of time), the samples in the capsule containing the most water had the largest combined weight loss. Again comparing two sets of samples heated for the same length of time (15 and 16 or 17 and 18), the set whose granodiorite sample showed the larger weight loss relative to the other had a relatively smaller loss in the argillite sample. This latter result may imply the existence of some type of "buffering" phenomenon, but the complexity of the system and doubts about the data do not allow any further conclusions.

C. Chemical Analysis Data

The results of chemical analyses for calcium, potassium, sodium are presented in Tables VI-2, -3 and -4. The uncertainties have been discussed above in section V and are given as plus-or-minus figures in the tables. It is seen that if indeed there are any changes in the concentrations of these elements, they are quite small. Though the sample materials

Table VI-2. Analytical results for Calcium

	Granodiorite			Argillite		
Experiment No.	Ca content before, weight %	Adjusted for weight loss	Ca content after, weight %	Ca content before, weight %	Adjusted for weight loss	Ca content after, weight %
14				1.65±.025	1.74	1.665±.025
15	1.19±.02	1.24	1.21±.02	1.65±.025	1.70	1.675±.025
16	1.19±.02	1.22	1.21±.02	1.65±.025	1.72	1.71±.025
17	1.19±.02	1.26	1.25±.02	1.65±.025	1.66	1.65±.025
18	1.19±.02	1.22	1.235±.02	1.65±.025	1.70	
(18-A-1)						1.64±.025
(18-A-2)						1.695±.025
(18-A-3)						1.73 ±.025

Table VI-3. Analytical results for Potassium

	Granodiorite			Argillite		
Experiment No.	k content before, weight %	Adjusted for weight loss	k content after, weight %	k content before, weight %	Adjusted for weight loss	k content after, weight %
14				3.81±.08	4.015	3.83±.08
15	2.84±.06	2.97	2.93±.06	3.81±.08	3.93	3.86±.08
16	2.84±.06	2.90	2.88±.06	3.81±.08	3.98	3.79±.08
17	2.84±.06	3.00	3.08±.06	3.81±.08	3.83	3.43±.07
18	2.84±.06	2.91	3.01±.06	3.81±.08	3.93	
(18-A-1)						3.47±.07
(18-A-2)						4.01±.08
(18-A-3)						3.94±.08

Table VI-4. Analytical results for Sodium

	Granodiorite			Argillite		
Experiment No.	Na content before, weight %	Adjusted for weight loss	Na content after, weight %	Na content before, weight %	Adjusted for weight loss	Na content after, weight %
14				1.505±.06	1.59	1.53±.06
15	3.70±.11	3.85	3.735±.11	1.505±.06	1.55	1.375±.05
16	3.70±.11	3.77	3.535±.11	1.505±.06	1.57	1.42±.09*
17	3.70±.11	3.90	3.835±.12	1.505±.06	1.51	1.22±.05
18	3.70±.11	3.78	3.595±.11	1.505±.06	1.55	
(18-A-1)						1.225±.05
(18-A-2)						1.66 ±.07
(18-A-3)						1.54 ±.06

* Duplicate analyses for this sample gave 1.335 and 1.51 wt % Na. Time did not permit a third analysis

were chosen with the intent of "buffering" the system in its major components, the weight losses cannot be accounted for in terms of changes in the concentration of the three elements studied.

The argillite sample in experiment 18 was larger than usual, and was split into three sections for separate analysis. The three sections are numbered 18-A-1, -2, -3, starting from the gold foil (unsealed) end of the small capsule; i.e. 18-A-3 was the hot end of the sample. The division was roughly into thirds. Some material was lost in the division, so the exact weights of the three sections were unfortunately not measured.

The calcium content of the samples did not change during the experiments. The agreement between Ca contents in analysis and those calculated from initial Ca content adjusted for weight loss is very good, except for sample 14-A. This sample was from an experiment completed just after a period of considerable difficulty with the pressure apparatus. As this problem caused leaks in the enclosing large capsule, the small sample containers were fitted with a new outer capsule and re-heated without emptying and re-weighing the sample inside. As this sample was fitted with several large capsules before the source of the pressure problem was discovered, some sample was probably lost along the way, causing the initial sample weight carried forward to be in error. This same discrepancy shows up in the sample's value for potassium.

The samples are also seen to be very close to the starting materials in potassium content. Argillite samples 16, 17, and 18-A-1 show a depletion in K which is just outside the range of analytical uncertainty, but normal uncertainty in the weight loss measurement

eliminates 16. Granodiorite samples 17 and 18 show a very slight enrichment in K. An increase in K in the granodiorite would differ from Orville's (1963) results, but the discrepancy could be explained in terms of the relative Ca contents of the two materials studied here.

The sodium results show no change in the Na content of the granodiorite, and, at best, a slight depletion in the argillite samples. Poor precision at low concentrations was such a problem that no conclusions can be made for those samples.

VII. DISCUSSION OF RESULTS

The primary conclusion is that if any transfer of calcium, sodium, or potassium took place in these experiments, it was too small to be demonstrated conclusively by the data presented here. The x-ray studies suggest some changes in the physical state of the sample materials, as would be expected from simple heating under pressure. Chemical changes in Na, K, and Ca content under the conditions of these experiments are, however, either quite small or non-existent. The samples that were heated for the longest time showed the onlyapparent change, suggesting that the duration of the experiments was too short.

Assuming that the results of the longer experiments represent the closest approach to equilibration, the data for these runs provide orders of magnitude for the changes these experiments were designed to produce. These limits may be useful in dictating the type of experiment or analytical procedures necessary to make quantitative conclusions about alkali metasomatic phenomena in geological systems represented by the materials studied here. For example, the largest changes in potassium content measured were on the order of ten percent of the amount of potassium present in the starting material. Thus any similar experiment to provide quantitative data must be designed to make meaningful measurements on changes that are as small or smaller than ten percent of the amount of potassium in the starting material.

The materials selected for this investigation had some potential for answering questions raised by Orville (1963) about the effect of calcite on K-feldspar porphyroblast formation and/or "metamorphic differentiation" in regional metamorphism. It is clear that the argillite samples (at the cold end of the thermal gradient) were not visibly en-

riched in potassium - in fact, the reverse may be true judging from the results of the longer experiments. Most of the calcite in the starting material was decomposed according to observations with microscope and x-ray diffractometer. As the calcium content of the argillite did not change, it is assumed that the CaO liberated entered the plagioclase feldspar phase. Looking objectively at the sodium and potassium analytical results, neither type of sample showed significant enrichment or depletion in Na or K under the conditions of these experiments. Hence no evidence is offered for or against expectations for such a system.

With reservations about uncertainties in the analytical data in mind, some calculations have been made using the numbers from the tables in section VI. Table VII-1 shows the weight fraction data recalculated to mole percent, totalling 100 in terms of Ca, Na, and K. This table shows that not only are the changes for the individual elements quite small (if they indeed exist) but the changes for one element relative to the others are also very small.

From weight losses, calculations of the amounts of K and Na in the vapor phase were also done for a comparison with the data of Orville (1963). The results for the available data are as follows:

Experiment No.	K/(K+Na) in vapor, mole fraction	Mole percent
15	0.170	17.0
16	0.225	22.5
17	0.324	32.4

These numbers are of the same order of magnitude as those of Orville, but are not directly comparable as experimental conditions were different. There is probably no difference between the numbers for experiments 15 and 16. There may be a difference between those two

Table VII-1. Molal composition of samples in Ca-Na-k system, recalculated to total 100%

	Granodiorite			Argillite		
Sample No.	Mole % Ca	Mole % k	Mole % Na	Mole % Ca	Mole % k	Mole % Na
Starting materials	11.28	27.61	61.12	20.17	47.75	32.08
14	(no data for granodiorite)			20.15	47.56	32.29
15	11.49	27.95	60.56	20.87	49.29	29.84
16	11.72	28.60	59.68	21.20	48.14	30.65
17	11.27	28.47	60.25	22.61	48.23	29.16
18	11.67	29.15	59.19			
(18-A-1)				22.37	48.51	29.12
(18-A-2)				19.48	47.27	33.25
(18-A-3)				20.47	47.78	31.75

and the number for experiment 17, suggesting that the amount of K in the vapor phase increased with time.

The same calculation showed that the maximum loss (by weight) of K plus Na was for sample 17-A: 0.92 milligrams. This sample happened to be the one showing the minimum weight loss (0.59 mg), but normal losses were three to eight milligrams. Hence the vapor phase must have contained a considerable amount of the other components in the system.

Perhaps the most interesting result of the analyses was the observed variation in the composition of the three sections of the argillite sample from experiment 18. The calcium content of the other samples was observed to be unaffected by exposure to the vapor phase. Thus some other mechanism is implied for movement of Ca within the small sample capsule. The movement observed here is toward the heat source: the cool end is depleted slightly, the middle section contains the expected amount, and the hot end is very slightly enriched.

Dennen (1951) studied variations in chemical composition across igneous contacts in field occurrences. In the occurrences studied which suggested a large thermal gradient, he noticed wave-like disturbances in the concentrations of most elements near the contact. He also suggested that opposed concentation and thermal gradients (such as the situation simulated in the present experiments) might set up rather complex migration phenomena.

The data from his study is not comparable to that presented here, but the suggestion of a "wave-like disturbance" in the concentrations of different elements is of interest. Though the uncertainty in the analyses here preclude any conclusions, the analytical results for sodium

and potassium do show maxima in the middle section of the argillite sample from experiment 18. These maxima would indicate movement of material toward the heat, as well as out of the sample through the cooler end.

If there is indeed some movement of atoms toward a heat source, some mechanism other than the chemical one of diffusion in response to a concentration gradient must be proposed. The possibility of some type of mechanical movement in response to heat flow raises some interesting questions deserving of further study.

VIII. SUGGESTIONS FOR FURTHER STUDY

Several immediate improvements could be made on the experiments reported here. In light of the uncertainties in the chemical analyses, well-analyzed rock samples such as G-1, W-1, or one of the new U.S.G.S. standard rock samples should be used as starting materials. Interpretation of results for such small chemical changes would be considerably less difficult if the original compositions of the samples were known with a higher degree of certainty. For example, if the four numbers for the Na contents of the "reacted" granodiorite samples from Table VI-4 are simply averaged, they yield 3,68 weight percent Na. The value used for the Na content of the starting material was 3.70%, based on 6 analyses ranging from 3.63 to 3.77%. Though three of the four sample results were outside this range, it is not really known whether the cause is contact metasomatism or statistics.

Another improvement would be to use a chloride solution for the vapor phase, instead of pure water. This step is apparently justified by natural occurrences in inclusions, etc. Judging from the lengths of the present experiments compared to Orville's (1963), the Cl ion must have produced a more rapid attainment of equilibrium. As the longer experiments in the prsent series produced slightly larger differences in the concentrations of the elements measure, it is assumed that equilibrium was lacking in the shorter runs at least, and possibly even in the longer ones.

The weight-loss technique as used here is considered inadequate for quantitative inferences about the vapor phase because of the practical difficulties described above. Direct study of the aqueous phase, as done in Orville's (1963) experiments, is considered superior, primarily because his technique does not involve inference from measurements which are likely to be in error by a large fraction. A problem that was

inadequately faced in both techniques was that of possible precipitation of vapor-soluble residues when the sample was quenched. Orville (1963) approached this problem by washing his samples with water after quenching. However, if silica or alumina are principal components of the vapor phase, such residues are likely to be water-insoluble. The suggestion would be to try to make measurements of the magnitudes of these changing solubilities to see if this effect is indeed a problem in interpreting the results of experiments. Such measurements have been made for pure silica (see, for example, Kennedy, et. al., 1962) but, to the present author's knowledge, do not exist for other rock-forming components or, more importantly, combinations of those components (Tuttle and Bowen - 1958 - made some indirect measurements in the system $NaAlSi_3O_8$ - $KAlSi_3O_8$ - SiO_2 - H_2O, but "no quantitative data on feldspar solubilities were obtained.").

The experience gained in the investigations reported here suggests several different lines of further study. Further work on contact metamorphic and metasomatic phenomena should be divided into: 1) quantitative investigations of the chemical changes involved in contact metamorphism; 2) petrologic studies of mineral assemblages produced when natural materials are heated together in the presence of a vapor phase; and 3) exploratory experimental investigations of the mechanisms of heat transfer.

If quantitative measurements of the chemical changes in contact metamorphic phenomena and metasomatic phenomena are to be made, the first problem is precise knowledge of the compositions of the starting materials. The use of analyzed standard rock samples has been suggested above, and synthetic materials offer another possibility. A more informative

approach, however, would be to perform a series of experiments, starting with basic mineral components of rock types of interest - as the alkali feldspar in Orville's (1963) experiments - then adding other mineral components one at a time until the mineralogical compositions of particular rock types were approached. Consider, for example, the two rock types studied in the experiments for this thesis. The initial samples should both be quartz and plagioclase feldspar in relative amounts approximating those in the natural materials. Those samples could be heated under pressure with a temperature gradient. Alkali feldspar of known composition would then be added to about 20 modal percent in new samples of "intrusive" and "country rock" and the heating experiment run again. Successive experiments would involve addition of calcite and muscovite to the "country rock" samples and biotite plus other accessories of interest to the "intrusive" samples. Combined chemical analysis and petrologic data from such a series of experiments should allow some definite and reasonably quantitative interpretations of mass-transport/chemical-change phenomena in a particular geologic environment.

Another approach would be to simply study the mineral assemblages produced in a simulated contact metamorphic environment. The experiments on dolomite and aplite cores described in Appendix I demonstrated that the presence of a temperature gradient may have a pronounced effect on mineralogy, though the chemistry of the system as a whole remains constant. Information on a variety of rock types and their mineralogical interactions under a specific set of experimental conditions could be compiled relatively easily using an x-ray diffractometer as the only analytical tool. Semi-quantitative information on phase

assemblages as functions of pressure, temperature, and temperature differential could be compared to stability-curve data for specific mineral systems to test the effects of the temperature gradient and the presence of other components. Crushed rock samples are recommended over the cores used in the experiments described in the appendix for expediency in the attainment of equilibrium. Dennen (1951) suggested that the mechanism for alteration by the vapor phase is via hydrated ions moving along grain boundaries. Crushing merely exposes a larger amount of free surface area for this migration.

A different question for further study is the possibility of movement of atoms - either chemically or mechanically - in response to heat. The results of the calcium analyses for one of the samples in this thesis is suggestive of some redistribution of this type. Dennen's (1951) field studies also offer some interesting phenomena to be explained. A contact between a diabase dike and a rhyolite "country rock" showed maxima for several major elements in the rhyolite at or near the contact. This occurrence is representative of a contact across which both thermal and concentration gradients were present, but the intrusive species probably lacked a vapor phase to serve as a medium for chemical diffusion. A contact between a granite and a shale showed similar maxima in the "country rock" near the contact, but also showed "perturbations" on these maxima, possibly due to the chemical alteration effects of an invading aqueous vapor phase. In this instance, thermal and concentration gradients were present, and the effects of reciprocal reaction with the invading vapor appear to be superposed on a gentle migration in response to heat flow.

To the present author's knowledge, the mechanics of heat transfer

are always treated in terms of conduction, utilizing estimates of thermal conductivities, diffusivities, etc., for geologic materials at the temperatures in question (see, for example, Jaeger - 1964). With very limited knowledge of the field, the author can make no suggestions but would be interested to see a series of experiments measuring the amount of heat actually transferred between natural geologic materials at temperatures on the order of 1000°C. Comparison of such measurements with calculations could yield interesting results about effects of grain size, mineralogical composition, and other lithologic features on the amount of heat conducted through a rock.

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APPENDIX I. EXPERIMENTS WITH APLITE AND DOLOMITE

The first experiments in this series were with small cores (2.4 mm. in diameter) from blocks of the Mount Katahdin (Maine) aplite and the Blair dolomite. Several exploratory constant-temperature tests were made to locate the pressure and temperature conditions of interest in Bowen's (1940) decarbonation series. Then two experiments were made to observe the effect of a temperature gradient on the mineral assemblages produced by heating these rocks together.

The procedure for the constant-temperature experiments was to seal the two cores in physical contact inside a small gold capsule about 5 cm. in length. Demineralized water was added with the cores in an amount roughly equal to 10% of the weight of the aplite core. The sealed capsule was then heated at 1 kilobar pressure in an externally heated pressure vessel. The temperatures studied were between 650°C and 800°C, and the heating times were 5 to 30 days.

Below 750°C, there was little evidence of any reaction. At this temperature and above, however - where partial melting of the aplite had begun - the surface area of the dolomite showed considerable silicification. As determined by x-ray patterns, the silicic "crust" formed on the dolomite core was composed principally of calcite and forsterite. No quartz or other Ca-Mg silicate lines were visible in the x-ray record. The thickness of this crust was dependent on the distance from the "contact" with the aplite (thicker as

contact approached), and was somewhat affected by the length of time in heating. The effect of appreciably higher temperatures was not studied. The rest of the core beneath the siliceous coating was apparently unaffected dolomite. Several attempts were made to study a cross-section of one of these silicified cores, but the friability of the crustal material led to disintegration in the thin-section grinding process.

The aplite core after these experiments was quite porous, and the end away from the "contact" was often covered with glass, normally blue in color. X-ray patterns showed removal of all quartz lines, hence the glass was assumed to be mostly silica, possibly colored with some iron and/or magnesium. The x-ray patterns also showed some homogenization of the feldspars, which would be expected from heating. In a cross-section of one of these cores mounted on a slide and ground for microscope study, some of the hornblende grains showed some signs of deterioration. This deterioration is suggested as the source of whatever ion contributed the color to the silica glass.

The gold capsule usually also contained some loose flaky material that was not identified. This material is thought to be amorphous silica that was precipitated from the vapor phase during the quenching process.

Two experiments with the dolomite and aplite cores were made using a temperature gradient. Five-cm. cores of aplite and ten-cm. cores of dolomite were sealed in gold capsules 17 cm. long, along with demineralized water in an amount

roughly 10 percent of the weight of the aplite core. The capsules were then arranged in an externally heated "diffusion bomb" (described earlier) such that their aplite ends touched beneath the hottest point in the furnace. Temperature was measured with chromel/alumel thermocouples at 2.5 cm. intervals out to a distance of 10 cm. from the center in both directions. The maximum temperature was 800°C, and the gradients employed were 200°C and 250°C over a distance of 10 cm. The samples were heated at 1 kilobar pressure for six days.

The results were quite similar in both experiments. The aplite core had a porous appearance at the hottest end. X-ray diffractometer patterns for these sections showed removal of all quartz peaks, while alkali and plagioclase feldspar peaks remained. Further down towards the cooler end, clear, hexagonal-prismatic crystals grew on the outside surface of the core. These crystals had all the habitual characteristics of quartz, and appeared to be growing on sites where quartz grains had been cut through in the coring process. There was no distinct division separating the regions of dissolution and precipitation, as there was a section (up to 1 cm. in length) where the quartz was dissolved out and re-precipitated about 90° laterally around the circumference of the core, with no displacement in the lengthwise direction. A slight circumferential temperature gradient in the heating apparatus is thought to be the cause of this feature.

The dolomite core had a thin coating containing a clear fibrous mineral. The optical properties of this mineral were very similar to those of wollastonite, except the refractive indices were somewhat higher: approximately 1.672, with very weak birefringence, as opposed to 1.620, 1.632, and 1.634. An x-ray diffractometer pattern of the coating showed it to consist of wollastonite and a smaller amount of calcite. Magnesia from the dolomite may have been the cause of the higher indices for the wollastonite, but some of this oxide is believed to have gone into hornblende, as discussed below.

The surfaces of the aplite core, and to a lesser extent the hot end of the dolomite core, had a limited covering of small, deep green crystals. These crystals showed yellow-to- green pleochroism and occurred in the pseudo-hexagonal aggregates of columnar blocks characteristic of synthetic hornblende. Hence, it is believed that this hornblende formed using some of the MgO from the dolomite, even though the majority of the crystals formed on the surface of the aplite core.

The presence of a thermal gradient appears to have affected the mineral assemblages in the system studied here. The primary rock-forming component in the vapor phase was obviously silica. This line of investigation was thus terminated in order to study the possibility of buffering the silica to observe relationships between other components in a simulated contact metasomatic environment.

APPENDIX II. PROCEDURE FOR DISSOLVING SAMPLES

While the samples were being dried, platinum dishes were thoroughly washed with scouring powder, then laboratory glassware soap. The dishes were then thoroughly rinsed several times with both two normal hydrochloric acid and demineralized water. As the last rinse was with demineralized water, drying the dishes was unnecessary, hence not done.

The weighed samples were put into the Pt dishes, and perchloric acid was added in the amount of 1 ml. $HClO_4$ for approximately 100 milligrams of rock sample (0.2 ml. for the 20 milligram samples used here). Next, 10 ml. of 48% hydrofluoric acid was added. The dishes were then placed on a steam bath for heating, and stirred occasionally with (individual) teflon stirring rods. The solution was evaporated down to near dryness. Then another 10 ml. portion of HF was added and the dish placed back on the steam bath. The HF additions were repeated until the sample was decomposed.

When the sample was dissolved and the last portion of HF had been evaporated off, enough 2N HCl was added to dissolve the residue (normally about 20 ml.). If everything did not dissolve in the 2N HCl, more HF treatments were done. If the sample did dissolve, the solution was evaporated to the $HClO_4$ again, and another portion (normally about 10 ml.) of 2N HCl was used to redissolve the residue.

The solution was then evaporated to near dryness; i.e., until most of the $HClO_4$ was gone. The sample then

consisted of Na, K, Ca, and Al perchlorates. These perchlorates were dissolved in 0.2N HCl and diluted to 50 ml. in volumetric flasks. From this primary solution, dilutions were made to get the elements of interest in the appropriate concentration ranges for analysis.

Primary solutions were stored in small (approximately 60 ml.) polyethylene bottles with screw-on caps to prevent evaporation. Different dilutions were made from the primary solutions for each of the three elements studied, except for the Na and K analyses on the argillite samples, for which the same diluted solutions were used. These dilutions were made as they were to be used, and were analyzed in batches for a particular element. None of the diluted solutions were kept more than two days, and most were diluted and analyzed on the spectrophotometer the same day.

APPENDIX III. LANTHANUM EFFECT ON CALCIUM DETERMINATION

The atomic absorption analytical method is afflicted by several types of interferences, often peculiar to different elements. One of these, called "chemical interference", results from chemical combination of the element of interest with other elements in the solution. Angino and Billings (1967, p.42) have collected reports of interference with calcium determination by sulfate, phosphate, alumina, and silica - apparently a Ca-Al or Ca-Si complex is formed. For the present analyses, Si was removed by dissoving the sample with HF, $SO_4^=$ was not added in dissolution, and $PO_4^=$ was assumed to be present only in quantities too small to affect the Ca determination. Hence the problem was with Al.

The calcium can be released by addition of a large amount of a competing cation, most often lanthanum. The Perkin-Elmer manual (1964) recommends that all standards and all solutions be made up to contain 1% La (weight/volume). This concentration should protect the Ca determination from as much as 1000 micrograms/ml Al. Angino and Billings (1967, p.99) also suggest adding enough La to give all solutions a La/Al ratio greater than 10.

Lanthanum is, however, not only quite expensive, but detrimental to the operation of the spectrophotometer as it clogs the burner and/or coats the optic surfaces with La_2O_3. W.H. Pinson and P. Kolbe experimented with lower concentrations and found that using 0.5% La solutions had no obvious effect

on Ca determinations. As a large number of Ca analyses were to be made for this thesis, further study was in order.

The first experiments were with a series of W-1 solutions. From each of two primary solutions, dilutions were made to 0.5, 0.4, 0.3, 0.2, and 0.1% La, with constant Ca content. The values obtained were all within ± 2% of the average (8.185% Ca), with the La concentration apparently having little or no effect. A G-1 solution was used as a standard. As Fleischer (1965, reporting the values of Suhr and Ingamells) reports 7.805% Ca for W-1, the conclusion was that matrix effects between G-1 and W-1 probably caused the five percent discrepancy.

W-1 is relatively high in calcium and low in aluminum. Thus, the above tests didn't mean much in terms of the La/Al ratio, as the lowest value of that parameter for the La concentrations studied was greater than 100. The next step was to test something with a much higher Al content relative to Ca. The material chosen was a National Bureau of Standards feldspar, their Standard Sample No. 99. This standard is a soda feldspar containing 0.257% calcium and 10.085% aluminum (NBS Circular No. 552, August 31, 1954).

Preliminary tests showed the break-point in the calcium determination came at a La/Al ratio of about 20. Further tests using G-1 with 0.5% La as a standard gave the following results for solutions of the same sample:

Solution No.	La content	Calculated La/Al	Wt.% Ca measured
54-3	0.5%	35.75	0.234%
54-4	0.3	21.45	0.228
54-1	0.3	17.8	0.218
54-2	0.2	11.85	0.183
54-5	0.1	7.15	0.151

The conclusion was a La/Al ratio of 20 or greater was necessary for freeing calcium determinations from this interference.

As standards and unknown solutions were all to be diluted to the Ca concentration best suited for analysis, the amount of Al relative to Ca was compared for standards and starting materials. The Mt. Airy granodiorite contained the most Al, so La concentration was figured to cover at 0.3%. This La concentration was used in standard and unknown solutions in all analyses for calcium.

Figure A-III-1. Effect of La/Al ratio on amount of calcium measured for NBS Standard Sample No. 99